REDUCTION OF Cd(II), Ag(II) AND Cu(II) USING RUBBER SEED SHELL : ADSORPTION ISOTHERM AND KINETICS

by

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ABSTRACT

Increasing industry in Malaysia produce high amount of wastewater, thus increase the heavy metal contaminants that become global concern of environment. Adsorption of heavy metals by activated carbon will need higher cost compare to the other adsorbents. Thus, an alternative way of waste utilization is initializing by researcher to reduce wastewater management cost. The objective of this research is to investigate the potential of rubber seed shell as alternative adsorbent to reduce Cd(II), Ag(II) and Cu(II) ions from aqueous solution by find its kinetic and adsorption isotherm using batch techniques. The adsorbent and adsorbate prepared is used for testing the effect of removal of the ions by the variation parameters of solution pH (pH2, Ph4,pH6 pH8,pH10), contact time (40min, 60min, 80min, 100min, 120min), adsorbent dosage (0.1g, 0.2g, 0.3g, 0.4g, 0.5g) and initial concentration (20ppm, 40ppm, 60ppm, 80ppm, 100ppm). The optimum ph=6, effective time and dosage of 120min and 0.3g is use through all parameters variation. All the experiments are using batch adsorption process and finalize by shake using rotary shaker and analyze using Atomic Absorption Spectroscopy (AAS). This adsorption case fit Langmuir isotherm with correlation coefficient of 0.9991 and satisfactory Pseudo-second order kinetic with correlation coefficient of 1 for all metal and adsorption constant range 0.0662 to 0.1873 g/mg.min. This research approved that rubber seed shell can be used as an alternative adsorbent to reduce Cd (II), Ag (II) and Cu (II) ions from aqueous solution.

PENGURANGAN Cd(II), Ag(II) DAN Cu(II) MENGGUNAKAN LAPISAN LUAR BIJI GETAH: ISOTERMA PENJERAPAN DAN KINETIK.

ABSTRAK

Industri yang semakin meningkat di Malaysia menghasilkan jumlah air sisa yang tinggi, seterusnya meningkatkan kadar logam berat di dalam air sisa yang menjadi pencemaran alam sekitar. Penjerapan logam berat oleh karbon aktif memerlukan kos yang lebih tinggi berbanding dengan adsorben lain. Oleh itu, alternatif karbon aktif dimulakan oleh penyelidik untuk mengurangkan kos pengurusan air sisa. Objektif kajian ini adalah untuk menyiasat potensi lapisan luar benih getah sebagai adsorben alternatif untuk mengurangkan Cd (II), Ag (II) dan ion Cu (II) daripada larutan akueus dengan mencari kinetik dan isoterma penjerapan. Adsorben dan bahan terjerap disediakan dan digunakan untuk menguji kesan penyingkiran ion oleh parameter perubahan pH larutan (PH2, pH4, pH6 pH8, pH10), masa (40min, 60min, 80min, 100min, 120min), dos adsorben (0.1g, 0.2g, 0.3g, 0.4g, 0.5g) dan kepekatan awal (20ppm, 40ppm, 60ppm, 80ppm, 100ppm). pH optimum = 6, masa yang berkesan dan dos yang efektif adalah 120min dan 0.3g digunakan. Semua eksperimen menggunakan penggoncang dan analisis menggunakan Spektroskopi Serapan Atom (AAS). Kajian penjerapan ini memenuhi isoterma Langmuir dengan nilai R^2 adalah 0,9991 dan kinetik Pseudo kedua nilai R^2 adalah 1 untuk semua logam dan pemalar 0.0662-0.1873 g / mg.min. Kajian ini membuktikan bahawa lapisan luar benih getah boleh digunakan sebagai bahan penjerap alternatif untuk mengurangkan Cd (II), Ag (II) dan ion Cu (II) daripada larutan akueus.

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LIST OF ABBREVIATIONS

AAS	Atomic Adsorption Spectrometer
Ag (II)	Silver (II)
Cd (II)	Cadmium (II)
Cu (II)	Copper (II)
g	grams
HCl	Hydrochloric Acid
L	liter
min	minutes
ml	milliliter
NaOH	Sodium Hydroxide
ppm	Part per million, mg/L
rpm	Rotation per minute
RSS	Rubber seed shell
t	Time

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LIST OF SYMBOLS

^{o}C	Degree celcius
C_e	Equilibrium concentration
C_o	Initial concentration
K_f	Freundlich constant
K_L	Langmuir constant
K_{1ads}	Rate constant of pseudo-first order
K_{2ads}	Rate constant of pseudo-second order
M1	Molarity
n	Heterogeneity factor
q_e	Amount of metal reduction over specific amount of adsorbent
q_m	Maximum adsorption capacity
q_t	Amount of adsorption at time
R^2	Correlation coefficients
V1	Volume

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Heavy metals in wastewater exhibit a global concern of environment due to its toxicity characteristics to many organisms (El-Ashtoukhy, Amin and Abdelwahab, 2008). Nowadays, heavy metal contaminants in industrial wastewater commonly in petroleum refining, mining activities, paint industry, pesticides and many more have become an anxiety environment issues al all over the world (Ngah and Hanafiah, 2008). Malaysia has been an industrial develop country which also go through with same environment problem that other countries experienced.

Heavy metals can be considered if it exists with density of 5g per cubic centimeter (Barakat, 2011). Cadmium (II), Silver (II) Copper (II) is an example of heavy metal that commonly exists in industrial wastewater. Cd (II) and Cu (II) commonly come from coatings industry wastewater (Santos, 2007) while Ag (II)

majorly from mines and quarries industries. Cadmium is an extremely toxic metal that leads to respiratory tract, kidney failure which may lead to fatal cause of renal failure by inhalation and may cause kidney, liver and bones fracture problem by ingestion. Copper metal and its alloy have been used over 1000 years. Although copper have been an essential needs in human health but it still can cause health problem to organism. One may experience irritation to nose, mouse and eyes which result dizziness, vomiting, diarrhea and stomachaches. In critical way, it may cause brain damage, renal damage and deposition in cornea. In the term of environmental, copper may interrupt activity in soils and activity of microorganism and earthworms. Silver very hazardous in case of eye contact (irritant) and severe over-exposure can result in death. Inflammation of the eye by silver is characterized by redness, watering, and itching.

In order to combat this problem, the traditionally used procedures for removal of metal is chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction (Johnson *et. al,* 2008). However, these techniques have certain disadvantages including incomplete metal removal, high reagent and energy consumption, production of toxic sludge or other waste products that require disposal. In other words, this traditional method is uneconomical and ineffective for concentration higher than allowable concentration. Thus, another method is discovering in this study to catch up with previous technology for metal removal. Adsorption process is selected in this study because it is effective and able to remove various levels of soluble heavy metals which is Cu(II), Cd(II) and Ag(II) in wastewater. Lately, interest has been focused on using low cost adsorbents or materials especially

agricultural by products for the removal of heavy metal from industrial wastewater (Wong *et. al*, 2003). Several bio sorbents such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk have been used for the treatment of metals in aqueous solution (Barakat, 2010).

The benefits including environmental benefits from the reuse of solid waste which is rubber seed shell for this study have been investigate to evaluate its potential for the treatment of heavy metals in wastewater. In this current investigation, the potential of rubber seed shell has been assessed for the removal of metal ions such as silver, cadmium and copper. In the other hand, this study also investigates the effect of Ph solution, contact time, adsorbent dosage, and initial concentrations. The purpose of this research is to assess the probability of implementing rubber seed shell as adsorbents for the adsorption of heavy metals in wastewater by applying the deviation of certain parameters.

1.2 Problem Statement.

Heavy metals from Malaysia industrial wastewater discharge into the ecosystems including rivers and seas will cause water pollution if the effluents are not properly treating. In spite of that, the situation will increased the heavy metal contaminants in ecosystems and directly increased the wastewater management cost in plant. In addition, the use of commercial activated carbon is high cost and energy

consumptions. Thus, an unconventional of low cost adsorption system is investigate using rubber seed shell (RSS) that shows good precursor for activated carbon and was an attractive source in producing high capacity activated carbon (Sun and Jiang, 2010). If the effluents are not suitable treated the company will need higher cost for the treatment.

In spite of that, Malaysia has become a rapid growth rubber country. According to the association of natural rubber producing countries, Malaysia is estimated own about 1,229,940 hectares of rubber plantation which resulted about 355,200,000 kg fat and 136,800,000 kg protein waste per year from rubber seed shell (Eka, Tajul and Wan Nadiah, 2010). This shell of *Hevea Brasiliensis* is said to be one of many agricultural waste which has become an environmental problem. Rubber seed shell can found at any rubber tree plantation areas such as Pahang which have the largest rubber plantation area followed by Johor, Perak, Kelantan and other state.

Thus, the purpose of this study is to investigate the probability of implementing rubber seed shell as adsorbents for the adsorption of heavy metals in wastewater by applying the deviation of certain parameters. This study focused on its adsorption kinetic data and the best fits equilibrium adsorption data using Isotherm Langmuir.

1.3 Objective.

- To reduce Cadmium (II), Silver (II) and Copper (II) by using rubber seed shell as adsorbent. In order to reduce these metals, a batch adsorption process is chose due to its easy and simplest method. Cadmium (II), Silver (II) and Copper (II) was added with rubber seed shell as adsorbent and some parameters was varied to get the results.

- To find the kinetic and isotherm Langmuir by implementing rubber seed shell as adsorbent for Cadmium (II), Silver (II) and Copper (II). Kinetic and isotherm Langmuir is important in adsorption because it described the mechanism of adsorption process and evaluated the value of maximum adsorption capacity using related equations.

1.4 Scope of the Study.

- This study was done to observe the reduction of Cadmium (II), Copper (II) and Silver (II) from aqueous solution using rubber seed shell as adsorbent. The reduction of Cadmium (II), Copper (II) and Silver (II) from aqueous solution was observed in term of its removal efficiency using the optimum operating condition determined.

- Observation and investigation of the effect of process condition for Cadmium (II), Silver (II) and Copper (II) that can be removed by using rubber seed shell. During the experiment, the parameters were observed and the equilibrium point for each parameters is used for further investigation.
- Determination Cadmium (II), Silver (II) and Copper (II) removal efficiency by analyzing the result of initial and final concentration for each manipulated variable using Atomic Absorption Spectrophotometer. The manipulated variables for this study are solution pH (pH 2, 4, 6, 8 and 10), contact time (40, 60, 80, 100, and 120 minutes), dosage of adsorbent (0.06, 0.12, 0.18, 0.24 and 0.30 grams) and initial concentration of adsorbate solution (20, 40, 60, 80 and 100 ppm)
- Determination of Langmuir adsorption isotherm and kinetic for Cadmium (II), Silver (II) and Copper (II) that can be removed using rubber seed shell as low cost adsorbents which is rubber seed shell.

1.5 Rationale and Significance.

This study is conducted to remove heavy metal ions including Cd (II), Ag (II) and Cu (II) which has become a global concern in terms of environmental and wastewater aspects. Adsorption is a process one or more component of liquid stream adsorbed on the surface of solid adsorbent and separation is accomplished (Geankoplis, 2003). In this study, rubber seed shell acts as adsorbents while the heavy metals are the adsorbate (adsorbed material). Physical and chemical methods are available for heavy

metal removal but it was quite expensive and ineffective. Hence, many research and study is conducted previously to find other natural resources which is using biological methods that could be an alternative methods. Other agricultural waste materials such as tea waste, rice husk, coconut husk, oil palm fibre, orange peel ,sawdust, jackfruit peel, peanut husk and many more are an example of low cost agricultural waste instead of rubber seed shell which available in Malaysia.

The usage of agricultural waste materials as an adsorbent is the only way to reduce agricultural waste instead of reducing pollution. Rationally, the rubber plant product including rubber latex and leaves is used in industry, so the rubber seed are the waste of the rubber plant. This study will reduce environment pollution by the usage of rubber seed shell in wastewater treatment and make rubber plant waste become a useful material that will give benefits to industrial and other sectors in Malaysia. Rubber seed shell is choosing in this research because of its moisture, volatile matters and fixed carbon characteristics that can replaced a conventional activated carbon adsorbents according to Sun and Jiang, (2010). Besides that, rubber seed shell also effective for variation concentration, economically practicable and easily to found as waste product at rubber production and plantation areas. In the other hand, rubber seed shell could be good adsorbents for the removal of heavy metals instead of being an agricultural waste that may increase environmental pollution in Malaysia and other rubber growth country. Besides that, this research also aims to convert waste to wealth.

CHAPTER 2

LITERATURE REVIEW

Excessive level of heavy metals that are discharged to the ecosystem become global issues and concern nowadays (Oszoy *et. al*, 2008; Johnson *et. al*, 2008 and Fu *et. al*, 2011). Commonly there are several metals that have been classified as toxic metals if they are emitted to the environment in quantities that pose risks which including Cadmium (Cd), Nickel (Ni), Copper (Cu), Zinc (Zn), Lead (Pb) and many more (Barakat, 2011; Johnson *et. al ,2008* ; Ngah and Hanafiah, 2008). This global issue considered risky because of rapid industrialization and it may cause several health problem to human instead of defect flora and fauna especially to Malaysia. These heavy metals commonly come from industrial wastewater that is not properly treating.

Although, heavy metals have many applications to domestic use but the release of these metal may effects human health together with ecosystems (Ozsoy *et. al*, 2008; Fu and Wang, 2011). Cadmium is not an essential to human life. A study by Bernard (2008) investigate that cadmium is well retained in human body as it was absorbed.

Thus, it may cause damage to kidney especially proximal tubular cells as well as bone demineralization and increase the risk of lung cancer. Copper is a chemical element or soft metal with good conductivity. Instead of cadmium, copper also accumulate in human body. It may cause gastrointestinal disturbance, irritation of the nose, mouth and eyes and it causes headaches, stomach aches, dizziness, vomiting and diarrhea. Besides, copper also will cause damage to kidney, lung and eyes. Over exposure to silver may lead to the decreased of blood pressure, diarrhea, stomach irritation and decreased respiration. In addition, long-term inhalation or ingestion of soluble silver compounds may cause agrarian.

2.1 Activate Carbon as Adsorbents.

Activated carbon is coal-based adsorbent that is widely used in industry to remove heavy metal from wastewater (Fu and Wang, 2011). Even though the use of activated carbon is efficient and well establish but it was expensive compared to other adsorbents, so, many researchers investigated a way to reduce the cost of activated carbon by add additives to the activated carbon such as alginate, tannic acid, magnesium and many more. Activated carbon has excellent adsorption properties which have been characterized by high specific area (Lo *et. al*, 2011). In spite of that, activated carbons have been use extremely because of its ability to removed variety types and amounts of heavy metals. Activated carbon is confirmed to be more efficient in term

heavy metal removal but less efficient in term of cost consumption compare to agriculture waste adsorbents.

2.2 Agriculture Waste as Adsorbents.

The use of activated carbon will cost a much compare to other adsorbents. Thus, researchers keep a research on searching appropriate adsorbents which using agriculture waste as adsorbents. A study by Wong (2003) investigates the potential of modified rice husk as adsorbents. The study agreed that the modified rice husk by column closely with the levels of batch equilibrium studies. Besides that, *bagasse* (an agricultural waste from sugar processing) were also have been studied the usage as adsorbents by Mohan and Singh (2002) which shows that the heavy metal removal capacity is increase as the temperature is increase and the data fits both Freundlich and isotherm Langmuir. The isotherm data and mechanism is achieved by using the same manipulated variables as this study. A similar agricultural waste as rubber seed shell also has been investigated. They are including cocoa shell, hazelnut shell and pecan shell (Johnson *et. al*, 2008). Each of these adsorbents shows different results, isotherm data and heavy metal removal potential. In spite of that, rubber seed shell is target to have similar results like other low cost adsorbent before since rubber seed shell is estimated 300kg/ha which is easy to found (Eka, Tajul and Wan Nadiah, 2010).

CHAPTER 3

MATERIALS & METHODS

3.1 Materials.

This study main material is rubber seed which come from Pahang state rubber plantation area. The chemicals involved in this study are Cadmium (II) sulphate, Silver (II) sulphate, Copper (II) sulphate, sodium hydroxide and hydrochloric acid. Cadmium (II) sulphate, Silver (II) sulphate and Copper (II) sulphate purchased from sigma Aldrich and used as an adsorbate for this adsorption study. Sodium hydroxide and hydrochloric acid was used to control pH during all experiment was get from University Malaysia Pahang chemical engineering laboratory.

3.2 Overall Methodology Flow Chart.

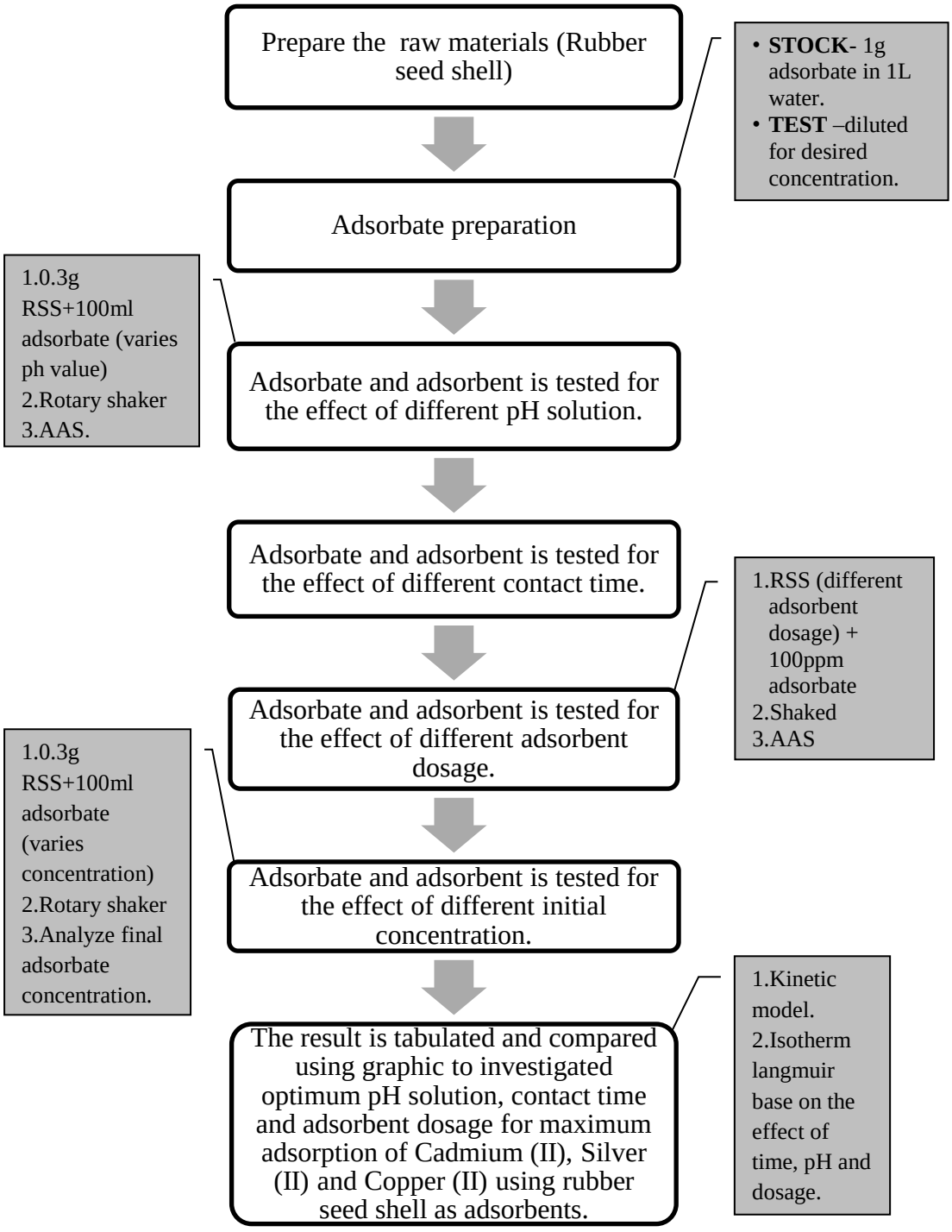

Figure 3.1: Overall flow chart for experimental methodology.

3.3 Experimental Methodology.

3.3.1 Rubber Seed Shell.

The study of heavy metal removal from wastewater used rubber seed shell as the main materials. Rubber seed shell was obtained from rubber plantation areas in Pahang state. Wash the rubber seed shell with deionized water, to remove dirt and impurities. The rubber seed shells were dried in the open air and grinded. The grinding product in form of powder was sieved using a laboratory sieve and the 160 μm portion was separated. This portion was washed with deionized water several times until the wash DI water was free of colour and turbidity. The clean powders proceed to oven at 80 ˚C to be dried and kept it in a sealed polythene bag. This step is important to make sure the powder kept in fresh for the next procedures.

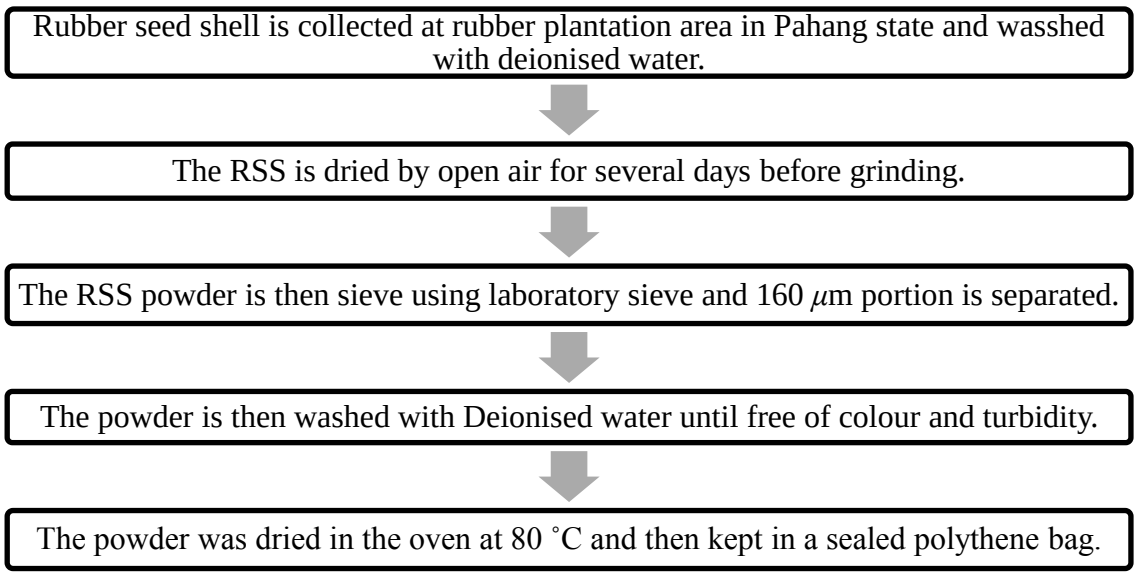

Figure 3.2: Flow diagram of preparation of rubber seed shell (RSS)